

NOTES ON THE DEVITRIFICATION OF OLD GLASS.—By H. RITCHIE  
CHIPMAN, M. A., Ph. D., F. C. I. C., and DOUGLAS Mc-  
INTOSH, M. A., D. Sc., Dalhousie University, Halifax, N. S.

(Read 14 December, 1925)

It has been generally supposed that the devitrification of glass is a phenomenon similar to that studied by Tammann (*Zeitn. Electrochem.* 10: 532, 1904), Guertler, (*Zeit. Anorg. Chem.* 40268, 1904) and others, which depends on the formation of crystal nuclei from which crystallization proceeds.

The devitrification of glass as a surface phenomenon has been explained by Albert Germann (*J. A. C. S.* 43:11, 1921) as follows. There is always a film of moisture on glass in equilibrium with the atmosphere. The silicates of the glass are in equilibrium with this film and must be more or less hydrolyzed depending on the condition of the glass, so that we may assume the presence of silicic acid, calcium hydroxide, and sodium hydroxide. The bases, however, absorb carbon dioxide and are converted to the acid carbonates. When the glass is heated the absorbed moisture is driven off, the silicic acid becomes dehydrated and roughens the surface. The separated silica forms an infusible coating over the surface of the glass which may under certain conditions dissolve in the underlying silica and the surface clear up, or under other conditions yield difficultly fusible calcium silicate in which case well defined crystal surfaces appear.

Germann took some old glass which showed a tendency to devitrify when heated and removed the surface layer by washing with hydrofluoric acid. If the devitrification was entirely due to the conditions of the surface its removal should destroy the tendency towards devitrification. Germann found this to be the case and suggests that old glass may be easily worked in the blast lamp flame if it is previously washed with hydrofluoric acid.

All of this work had been done with old glass which had been worked in the blast lamp flame and no mention has been made of glass devitrifying at lower temperatures. One of the

students at Dalhousie University had occasion to carry out a vapour density determination with a Dumas bulb, and was amazed to find that the bulb became heavily frosted at the temperature of boiling water. It was decided to test Germann's explanation to see if it applied to this case.

The Dumas bulbs in question were believed to be from twenty to thirty years old. They had not changed in appearance except that some of them had small crystals on their inner surface. Germann mentioned that old glass will show efflorescences of sodium carbonate, and it was found that a bulb with crystals gave an alkaline reaction when washed out with water.

One of the bulbs was fastened to a Toepler pump, surrounded by an electric furnace, and, having been exhausted, was heated to about 200°C. Shortly after heating the pressure rose from less than 0.01 mm to 0.2 mm. This was due to water vapour which was pumped off. The temperature was raised to about 450°C. and more gas was given off. The pressure finally reached an apparent maximum when the gas was pumped off and analysed. There was about 0.3 cc. and it proved to be practically all carbon dioxide.

A new bulb was kept in boiling sodium hydroxide solution and then placed in an oven at 120°C. It was thought that this treatment might remove the surface layer and prevent devitrification, but frosting occurred.

Following the suggestion given by Germann, another bulb was washed with hydrofluoric acid and then placed in an oven at 120°C. No devitrification occurred. The inside of the bulb was perfectly clear. According to Germann's theory the devitrification requires previous exposure to water vapour. As all the bulbs were sealed when made the inner surface was not exposed to the atmosphere, and hence no devitrification occurred on the inside.

A fresh bulb was partially washed with hydrofluoric acid and placed in the oven. It was found that only the parts of the surface which were not washed with the acid were devitrified.

A bulb was carefully broken into small pieces which were placed in a pyrex bulb and fastened to the pump. The system was exhausted and the bulb heated to 450°C, the pressure rising considerably. The gases were pumped off and were found to be about 50% carbon dioxide. On examination of the pieces after heating it was found that they were frosted on their outside surfaces only.

Some substances when heated will allow the passage of certain gases. It was observed that the devitrified bulbs did not permit the diffusion of any of the gases of the atmosphere when heated to 450°C. The fact that no diffusion took place when the glass was devitrified may be offered as additional evidence that the devitrification had only taken place on the surface, as it would have been expected to occur had the glass been crystalline throughout.

Germann states that the absorption of water from the atmosphere causes a tendency towards devitrification and that certain gases in the air of the laboratory may act catalytically. Apparently something like this has occurred in the case of the bulbs which has caused them to be so "weathered" that they will devitrify at 100°C. The results of these experiments are evidence that the devitrification of these bulbs is a surface phenomenon.